



Influence of alloying additives on the performance of commercial grade aluminium as galvanic anode in alkaline zincate solution for use in primary alkaline batteries

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Abstract

The self-corrosion of different grades of commercial aluminium such as 2S, 3S, 26S and 57S in 4 M NaOH containing 0.6 M ZnO has been determined by weight loss measurements. It is found that 26S and 57S aluminium exhibit negligible corrosion rates in the range $0.05\text{--}0.06\text{ mg cm}^{-2}\text{ min}^{-1}$, which can be attributed to the formation of a zincate coating on the aluminium surface. The influence of zincating on the performance of binary and ternary alloys of 26S and 57S aluminium obtained by incorporating alloying elements such as zinc, indium, thallium, gallium and tin as galvanic anode in 4 M NaOH containing 0.6 M ZnO has been examined by studying self corrosion, steady state open circuit potential, galvanostatic polarization and anode efficiency. It is found that zincated ternary alloys of 26S and 57S aluminium containing zinc and indium can serve as good galvanic anodes in alkaline medium. AC impedance measurements and X-ray diffraction studies have been carried out to understand the nature of the film formed on the aluminium surface.

1. Introduction

Aluminium possesses attractive properties such as high negative potential and high energy density in alkaline media and this, combined with its abundance, makes it an attractive choice as galvanic anode in primary alkaline batteries. But aluminium also has drawbacks such as a high rate of self-corrosion and gassing. This problem can be obviated by incorporating different alloying elements like indium, gallium and thallium in aluminium or by adding corrosion inhibitors, addition agents and complexing agents to the alkaline solution. It has been found that gallium, thallium and indium and a combination of these are advantageous in minimizing the corrosion of aluminium in alkaline solutions [1, 2]. The use of aluminium alloys containing a combination of indium, gallium and thallium as anodes in aluminium batteries has also been reported [3]. The utility of an aluminium alloy containing small amounts of phosphorous in addition to gallium or indium is also reported [4]. Mac Arthen [5] and Macdonald et al. [6] studied the performance of a few binary alloys of aluminium containing different percentages of indium, gallium and thallium. A commercially available Al–0.5% Mg alloy was examined in 7 M KOH electrolyte [7]. Extensive work has been carried out using different grades of commercial aluminium (99.0%), superpure aluminium (99.99%) and electrolytic grade aluminium (99.5%) and by incorporating different alloying additives such as

indium, gallium, thallium and zinc for studying their utility as galvanic anodes in alkaline primary batteries [8–10]. It has been observed that self-corrosion can be reduced to less than $0.1\text{ mg cm}^{-2}\text{ min}^{-1}$ by alloying Al with these elements.

Self-corrosion of aluminium of purity 99.5% in 4 M NaOH or 4 M KOH has been reduced by incorporating 0.6 M ZnO in alkaline media [11]. The influence of Hyamin (a quaternary ammonium compound) on the corrosion of aluminium in the absence and presence of zinc oxide was also studied. A mixture of sparingly soluble mercury complex and a soluble stannate and/or zincate salt was also found to inhibit the corrosion of aluminium in alkali [12]. Bohnstedt [8] has been able to achieve a shift in open circuit potential in the negative direction and an improvement in polarization characteristics of aluminium by incorporating mercury, indium and gallium ions in the alkaline solution. Ramachar and Sundararajan have inhibited the corrosion of aluminium in alkali using agar, gum accasia, dextrin, gelatin and glue [13]. The addition of 0.5 M sodium stannate to 5 M KOH solution has been found to inhibit the aluminium corrosion [14]. Various oxy-anions such as SnO_3^{2-} , $\text{Ga}(\text{OH})_2$, $\text{In}(\text{OH})_3$, MnO_4^{2-} , BiO_3^{2-} and their combination have been examined as inhibitors for the corrosion of pure aluminium (99.99%) in 4 M KOH [15]. The addition of nicotinic acid to an alkaline electrolyte is found to reduce the corrosion of aluminium and also the tendency of foaming of the alkaline electrolyte [16].

Kapali et al. [17] observed that wasteful self-corrosion of aluminium in alkali can be considerably minimised by incorporating a synergistic combination of Ca(OH)_2 and sodium citrate in the electrolyte. A combination of calcium with various organic compounds, like organic acids, ethers, amino acids etc. have also been tried as inhibitors for the corrosion of aluminium in alkaline solutions [18]. Sarangapani et al. [19, 20] observed that the incorporation of a combination of additives such as aluminium and zinc ions in the base electrolyte provides the formulation of a suitable battery electrolyte for use with commercial 2S aluminium as galvanic anode. John Albert et al. [21] have studied the influence of CaO , CaCl_2 and sodium citrate on the electrochemical properties of different grades of commercial aluminium in alkaline medium. Paramasivam et al. [22, 23] have observed that the formation of a zincate coating is very useful in reducing the self corrosion of different grades of aluminium to a negligible level of $0.04\text{--}0.08\text{ mg cm}^{-2}\text{ min}^{-1}$, while yielding high anode efficiency.

In the present study the influence of zincate coating on the performance of binary and ternary alloys of commercial grade aluminium as galvanic anodes in alkaline zincate solution has been studied using conventional techniques such as weight loss measurements, galvanostatic polarization studies, anode efficiency determination and a.c. impedance measurements. X-ray diffraction studies have also been carried out to understand the nature of the surface film.

2. Experimental details

2.1. Materials and solutions

Commercial aluminium of different grades such as 2S, 3S, 26S and 57S were used. These alloys were manufactured by the Indian Aluminium Company Ltd, Kolkatta and their compositions are given in Table 1. Indium (99.9% pure) and gallium (99.9% pure) were procured from Nuclear Fuel Complex, Hyderabad and Hydrometallurgy Division of Central Electrochemical Research Institute, Karaikudi, respectively. Zinc of 99.25% purity was procured from Binani Zinc Ltd, Aluwa, Kerala. Tin (99.5% pure) and thallium of L.R. quality were procured from SISCO Research Laboratory Private Ltd, Mumbai.

The sodium hydroxide was of reagent quality (E-Merck) and the zinc oxide (Loba Chemie, Mumbai) was

of 99% purity. All the solutions were prepared using distilled water.

2.2. Alloy preparation

Binary and ternary alloys of aluminium were prepared using a pit furnace fired by coke. The aluminium was melted in a graphite crucible and the desired amounts of various alloying elements were added to the molten aluminium in the crucible and stirred vigorously using a graphite rod. The molten alloy was poured into pre-heated graphite moulds to produce sheets 2 mm thick and rods of 8 mm diameter. The percentages of alloying elements in the cast alloys were confirmed by atomic absorption spectroscopy (AAS). The reproducibility of the chemical compositions of the alloys was established by casting not less than two batches of each alloy.

Rectangular strips of size $5\text{ cm} \times 2\text{ cm} \times 0.2\text{ cm}$ were used for self-corrosion studies. Open circuit potential measurements, anodic polarization studies and anode efficiency measurements were carried out on cylindrical rods, 8 mm in diameter with an exposed area of 50 mm^2 . These specimens were buffed with a cloth, polished with pumice powder and finally degreased with trichloroethylene.

2.3. Procedure

2.3.1. Determination of self corrosion rate

The weight loss method was used to compare the self-corrosion of different grades of commercial aluminium and their different alloys. Triplicate specimens were weighed and completely immersed in 200 ml of the test solution containing 4 M NaOH + 0.6 M ZnO for different durations of 120, 180, 240 or 300 s. At the end of each period, the specimens were removed, washed well with distilled water, dried, weighed and kept in a desiccator.

It was found that specimens dipped for 180 s received uniform and adherent zinc coatings. Coatings obtained after longer treatments showed poor adhesion and exhibited bulging, whereas those obtained following immersions for less than 180 s exhibited poor adhesion.

Specimens of different grades of commercial aluminium and their binary and ternary alloys were zincated as mentioned above and then immersed in 200 ml of the same solution for 7200 s at $30 \pm 1^\circ\text{C}$, then removed, thoroughly washed in tap water, dried and weighed.

Table 1. Composition of different grades of commercial aluminium

Aluminium grade	Composition (nominal)/wt %					
	Aluminium	Manganese	Magnesium	Copper	Silicon	Iron
2S	99.0	—	0.1	0.2	0.3	0.4
3S	97.8	1.1	1.1	—	—	—
26S	93.3	0.8	0.8	4.3	0.8	—
57S	97.7	2.0	0.3	—	—	—

2.3.2. Polarization measurements

Anodic polarization of zincated aluminium specimens and their alloys was carried out at 30 ± 1 °C using an in-house fabricated constant current generator with a Hg/HgO/4 M NaOH reference electrode and a 1600 mm² cylindrical platinum auxiliary electrode. Current and potential measurements were made using a high impedance multimeter (HIL). Polarization measurements were started after immersing the specimen for 1800 s in the test solutions, that is, once a steady state open circuit potential had been attained.

Current densities in the range from 1 to 100 mA cm⁻² were impressed on the working electrode and the steady potential was measured after 300 s at each current density. All measurements were carried out in stirred conditions to avoid concentration polarization and $E/\log I$ plots were drawn. The extent of anodic polarization of different grades of commercial aluminium and their binary and ternary alloys were noted.

2.3.3. Anode efficiency determination

Anode efficiency values were determined for six different current densities, namely, 25, 50, 75, 100, 125 and 150 mA cm⁻² using a cylindrical platinum electrode of 1600 mm² area for 7200 s. The solution was well stirred using a magnetic stirrer. After the experiment, the specimen was removed, washed well, dried and weighed. Anode efficiency was determined as the ratio of theoretical weight loss to observed weight loss. The experiment was repeated at least twice at each current density.

2.3.4. Impedance measurements

AC impedance measurements were carried out at the corrosion potential using an electrochemical interface (model 1186, Solartron, UK) and frequency response analyser (model 1174, Solartron, UK). Specimens of 26S aluminium dipped in 4 M NaOH alone and NaOH containing 0.6 M ZnO were used for measurements to examine the nature of the film formed during zincating. Nyquist plots were made from these experiments.

2.3.5. X-ray diffraction studies

Surfaces of the ternary alloy 26S aluminium containing zinc and indium dipped in 4 M NaOH alone and containing 0.6 M ZnO were examined using a computer controlled X-ray diffraction system (model JDX 803a, Jeol) having CuK_α (0.1541 nm) as the target material.

3. Results and discussion

3.1. Self corrosion studies

Table 2 gives values of self-corrosion rates for different grades of commercial aluminium in 4 M NaOH alone and containing 0.6 M ZnO. The extent of self-corrosion of different grades of aluminium in 4 M NaOH alone follows the order 3S > 2S > 26S > 57S. The difference in the extent of self corrosion shown by different grades of aluminium can be explained as follows.

Table 2. Corrosion rates of different grades of commercial aluminium in two test solutions, one containing 4 M NaOH and the other containing 4 M NaOH + 0.6 M ZnO

Aluminium grade	Self corrosion rate/mg cm ⁻² min ⁻¹	
	4.0 M NaOH	4 M NaOH + 0.6 M ZnO
2S	1.040	0.1520
3S	1.617	0.3360
26S	0.9325	0.0544
57S	0.8242	0.0565

Manganese, which is a cathodic impurity, is present in different percentages in different grades of aluminium as shown in Table 1. Thus 3S aluminium, having the maximum manganese content, shows maximum self-corrosion followed by 26S and 57S in decreasing order. Moreover, the presence of an anodic impurity, namely, magnesium in different percentages in 26S and 57S grades leads to cathodic polarization (cathodic protection) of the base metal aluminium resulting in lower self-corrosion of 57S than 26S. Similarly, the difference in corrosion rate between 26S and 57S grades can be explained on the basis of the number of cathodic impurities, namely, copper, iron and silicon.

Table 2 also gives the values of corrosion rates of different grades of commercial aluminium which were zincated for 1800 s and then dipped in 4 M NaOH solution containing 0.6 M ZnO. 26S and 57S grades show lower corrosion rates, that for 26S being the lowest. 2S and 3S grades showed very high corrosion rates and were not used for further studies. The better performance of 26S aluminium can be attributed to the presence of a significant amount of silicon (0.8%), which may interact with zinc present on the surface at the time of dipping in the alkaline medium, leading to the formation of zinc silicate on the aluminium surface [23].

Table 3 gives the values of self-corrosion rates of zincated binary and ternary alloys of 26S and 57S grades of aluminium in 4 M NaOH containing 0.6 M ZnO. It is found that both zincating and incorporation of alloying additives like zinc, indium and gallium have a combined influence in reducing the self-corrosion in alkaline zincate solution. The incorporation of zinc up to 3% is found to reduce self-corrosion, and then it increases marginally with increase in zinc content. Zinc is known to form a solid solution in combination with aluminium, its solubility in zinc being in the range 3.0–5.5%. Since the corrosion rate of zinc in highly alkaline solutions is very low (0.0014 mg cm⁻² min⁻¹ in 4 M NaOH) its incorporation in aluminium will reduce the self-corrosion. The binary alloys of both grades containing 3% zinc show minimum self-corrosion and serve as good galvanic anodes in alkaline media. The incorporation of indium in both grades of aluminium is found to be more effective than zinc. It is found that indium at a lower concentration of 0.025% is more beneficial than at higher concentrations. The influence of indium can be attributed to the higher cathodic overvoltage caused by its presence in the alloy, similarly to mercury and

Table 3. Corrosion rates of zincated 26S and 57S grades of aluminium and their binary and ternary alloys containing different percentages of alloying additives in 4 M NaOH containing 0.6 M ZnO
Duration of experiment 7200 s

Concentration of alloying additive /wt %	Self corrosion rate /mg cm ⁻² min ⁻¹	
	26S aluminium	57S aluminium
26S Al/57S Al alone	0.054	0.057
1% Zn	0.040	0.039
2% Zn	0.036	0.033
3% Zn	0.039	0.031
4% Zn	0.038	0.036
5% Zn	0.040	0.037
0.025% In	0.017	0.025
0.05% In	0.020	0.030
0.075% In	0.026	0.028
0.025% Ga	0.039	0.044
0.05% Ga	0.039	0.040
0.075% Ga	0.040	0.038
0.025% Tl	0.066	0.065
0.05% Tl	0.053	0.053
0.075% Tl	0.080	0.053
0.025% Sn	0.051	0.085
0.05% Sn	0.052	0.082
0.075% Sn	0.058	0.81
3% Zn + 0.025% In	0.011	0.019

gallium. The presence of indium is found to decrease hydrogen evolution which in turn influences the anodic reaction, that is, metal dissolution. Similar to indium, the incorporation of gallium also decreases the self-corrosion of aluminium in alkaline solution. As in the case of indium, a lower concentration of 0.025% is more effective than a higher concentration, but its incorporation is not so effective as that of indium. The incorporation of both thallium and tin in both grades of aluminium is found to have very little beneficial influence on their self-corrosion in alkaline zincate solution. So a close scrutiny of Table 3 clearly shows that binary alloys of 26S and 57S aluminium containing either 3% zinc or 0.025% indium are most suitable for use as galvanic anodes in alkaline media. Ternary alloys of 26S and 57S grades of aluminium containing 3% zinc and 0.025% indium show the lowest self-corrosion among the alloys reported in this study. Indium incorporated as the third element may be precipitated at grain boundaries and this is responsible for the better performance of Al–Zn (3%) In (0.025%) alloy in alkaline medium. Between the two ternary alloys that of 26S grade aluminium gives a lower corrosion rate than 57S grade.

3.2. Open circuit potential measurements

Table 4 gives the values of open circuit potentials of unzincated 26S and 57S grades of aluminium, zincated 26S and 57S grades of aluminium and their binary and

Table 4. Values of open circuit potential and the extent of anodic polarization for zincated 26S and 57S aluminium and their binary and ternary alloys in 4 M NaOH containing 0.6 M ZnO

Aluminium grade	Concentration of the alloying additive /wt %	Open circuit potential (V) vs Hg/HgO, OH ⁻	Extent of anodic polarization in mV at a current density of 100 mA cm ⁻²
26S (unzincated)	–	1.432	158
26S (zincated)	–	1.383	135
	1% Zn	1.383	120
	2% Zn	1.381	112
	3% Zn	1.380	108
	4% Zn	–1.378	114
	5% Zn	–1.378	118
	0.025% In	–1.382	109
	0.05% In	–1.381	115
	0.075% In	–1.380	118
	3% Zn + 0.025% In	–1.385	98
57S (unzincated)	–	1.430	132
57S (zincated)	–	–1.390	120
	1% Zn	–1.388	112
	2% Zn	–1.387	110
	3% Zn	–1.386	105
	4% Zn	–1.386	115
	5% Zn	–1.386	120
	0.025% In	–1.388	120
	0.05% In	–1.387	120
	0.075% In	–1.387	123
	3% Zn + 0.025% In	–1.389	102

Table 5. Values of anode efficiency of zincated 26S and 57S grade aluminium and their binary and ternary alloys in 4 M NaOH containing 0.6 M ZnO

Alloy composition	Anode efficiency/%					
	Current density/ mA cm^{-2}					
	25	50	75	100	125	150
26S aluminium	71	79	89	92	93	95
26S Al + 3% Zn	80	89	93	95	96	98
26S Al + 0.025% In	80	92	93	94	95	98
26S Al + 3% Zn + 0.025% In	81	93	94	95	97	99
57S aluminium	69	77	87	91	92	94
57S Al + 3% Zn	72	79	89	92	95	96
57S Al + 0.025% In	73	80	90	93	97	97
57S Al + 3% Zn + 0.025% In	75	81	92	93	97	98

ternary alloys containing zinc and indium in 4 M NaOH containing 0.6 M ZnO. It is found that zincating makes the open circuit potential less negative. This may be due to the formation of a zincate coating over the aluminium electrode, which then behaves like a zinc electrode. This, in turn, leads to a change in open circuit potential and a decrease in corrosion rate. As zinc and indium are cathodic to aluminium, their incorporation in aluminium in increasing concentrations makes the open circuit potentials of this zincated binary alloy less negative. But a combined incorporation of 3% zinc and 0.025% indium in both 26S and 57S grades of aluminium is found to make the open circuit potentials more negative. This observation can be explained as follows. Aluminium–zinc (3%) alloy has less tendency to form a strong oxide film than pure aluminium. Indium added as the third element may disrupt the protective oxide layer to such an extent that aluminium may become an unstable material in the presence of air. This makes it more active in corrosive environments and the open circuit potential becomes more negative [24].

3.3. Anodic polarization studies

Table 4 shows the extent of anodic polarization of zincated specimens of 26S and 57S grades of aluminium and their binary and ternary alloys containing different percentages of zinc and indium in 4 M NaOH containing 0.6 M ZnO. An increase in zinc content decreases the extent of anodic polarization of both 26S and 57S grades up to 3% zinc and a further increase in zinc content increases the extent of anodic polarization. Similarly, binary alloys of 26S and 57S aluminium containing 0.025% indium show less polarization than those containing more than 0.025% indium. The incorporation of both 3% zinc and 0.025% indium is found to be beneficial in improving the performance of both grades of aluminium as galvanic anodes, but more effectively that of 26S aluminium.

3.4. Anode efficiency determination

Table 5 gives the values of anode efficiency for zincated 26S and 57S grades of aluminium and their binary and

ternary alloys containing zinc and indium. The anode efficiency of these alloys is found to increase with increase in current density. It is found that the incorporation of both zinc and indium in 26S and 57S aluminium improves the anode efficiency, but more effectively in 26S.

3.5. Impedance measurements

Figures 1 and 2 give the Nyquist diagrams for the ternary alloys of 26S aluminium of 26S aluminium containing zinc and indium in 4 M NaOH alone and containing 0.6 M ZnO for the frequency range 10 Hz to 100 kHz at open circuit potential. It can be seen from Figure 1 that the impedance diagram has a near semicircular appearance. This shows that the corrosion

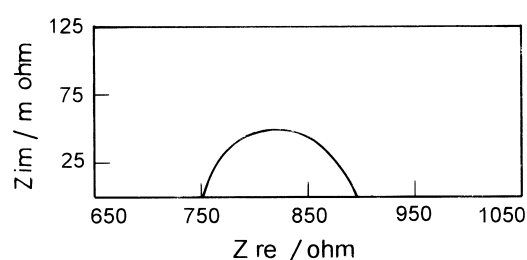


Fig. 1. Nyquist diagram for the ternary alloys of 26S aluminium containing zinc and indium in 4 M NaOH.

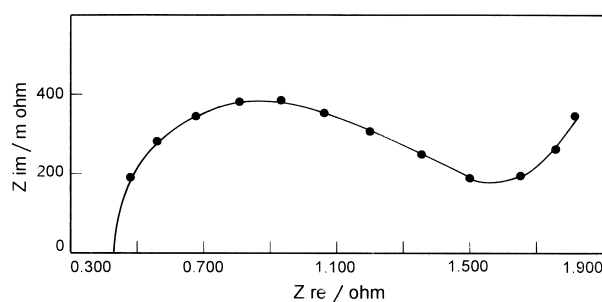


Fig. 2. Nyquist diagram for the ternary alloys of 26S aluminium containing zinc and indium in 4 M NaOH containing 0.6 M ZnO.

of the ternary alloy in 4 M NaOH alone is mainly controlled by charge transfer. It can be seen from Figure 2 that the distorted semicircle is followed by a linear region. A distorted semicircle indicates a charge transfer process occurring at the aluminium–electrolyte interface, during the Al corrosion. The low frequency branch is almost linear and makes an angle 45° with the real axis. This indicates a Warburg type impedance corresponding to a mass transfer process involving ionic diffusion. This situation arises when the electrode surface is covered with a reaction product of limited solubility [25].

3.6. X-ray diffraction studies

Figures 3 and 4 show X-ray diffraction patterns for the ternary alloy of 26S aluminium dipped in 4 M NaOH alone and that containing 0.6 M ZnO, respectively. The difference in peak heights observed in the patterns can be attributed to the formation of a zincate film on the aluminium surface.

A good galvanic anode should possess (i) minimum self-corrosion (ii) high negative open circuit potential (iii) less anodic polarization and (iv) high anode efficiency. Based on these requirements the ternary alloys of both 26S and 57S grade aluminium can serve as good galvanic anodes in 4 M NaOH solution containing 0.6 M ZnO. The ternary alloy of 26S aluminium shows a better performance.

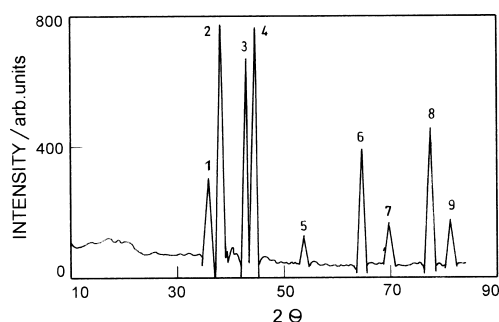


Fig. 3. X-ray diffraction pattern for the ternary alloys of 26S aluminium containing zinc and indium dipped in 4 M NaOH.

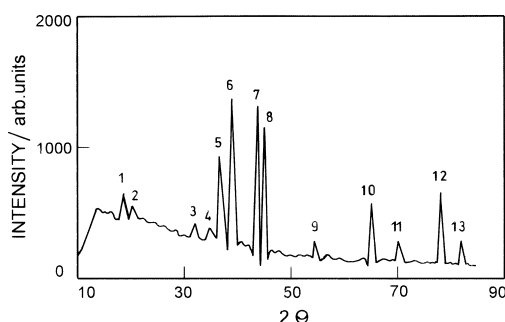


Fig. 4. X-ray diffraction pattern for the ternary alloy of 26S aluminium containing zinc and indium in 4 M NaOH containing ZnO.

4. Conclusions

The following main conclusions can be drawn:

- (i) The self-corrosion of different grades of commercial aluminium in 4 M NaOH solution alone follows the order $3S > 2S > 26S > 57S$.
- (ii) The self corrosion of different grades of commercial aluminium in 4 M NaOH containing 0.6 M ZnO follows the order $26S > 57S > 2S > 3S$.
- (iii) The decrease in self-corrosion of different grades of commercial aluminium in 4 M NaOH containing 0.6 M ZnO can be attributed to the formation of a zincate coating on the aluminium surface.
- (iv) Binary alloys of 26S and 57S aluminium containing either 3% zinc or 0.025% indium give lower self-corrosion rate and minimum anodic polarization.
- (v) Among the alloys studied, ternary alloys of 26S and 57S aluminium containing 3% zinc and 0.025% indium give the best performance as galvanic anodes in alkaline zincate electrolyte.
- (vi) 4 M NaOH solution containing 0.6 M ZnO is found to be the best electrolyte for 26S and 57S grades of commercial aluminium for use in alkaline primary batteries.

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